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Aluminum environments in synthetic Ca-Tschermak clinopyroxene ($CaAlAlSiO_6$) from Rietveld refinement, ^{27}Al NMR, and first-principles calculations

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ABSTRACT

^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR) and ^{27}Al triple quantum (3Q) MAS NMR spectroscopy have been performed at 21.1 Tesla (T), as a direct probe of environment around Al in synthetic Ca-Tschermak's clinopyroxene, $CaAlAlSiO_6$, henceforward referred to as CaTs. For comparison, ^{27}Al MAS NMR of CaTs has also been performed at 14.1 T. The ^{27}Al 3QMAS NMR spectrum of CaTs has revealed various local environments around octahedral and tetrahedral Al, both ordered and disordered, symmetrical, and distorted. Rietveld refinement of powder X-ray diffraction data has confirmed the high-temperature, long-range disordered $C2/c$ structure for this sample.

The ^{27}Al MAS NMR spectra of CaTs look broadly similar at 14.1 and 21.1 T. Both spectra exhibit two distinct peaks at the octahedral site and an irregularly shaped, broad tetrahedral site. The line widths are significantly broader at lower field and the ^{27}Al 3QMAS NMR spectrum at 21.1 T exhibits several additional peaks. At least three peaks were resolved at the octahedral site (in both the MAS spectrum along F2 and the 3Q spectrum along F1), whereas two peaks are clearly resolved at the tetrahedral site at 21.1 T. One tetrahedral peak, observed at both fields, is broad in F1 and narrow in F2, spread along the isotropic shift diagonal, indicating a highly disordered but relatively symmetric environment. The second peak, newly observed at 21.1 T, is narrow in F1 but very broad in F2, indicating an ordered but highly distorted environment. This peak has not been observed at lower magnetic field strengths.

Octahedral peak assignments have been made according to the number of Al atoms in the six tetrahedral sites around M1, where an increasing number of NNN tetrahedral Al (2Al, 3Al, and 4Al) is correlated with displacement of the chemical shift to higher frequency. Assigned sites are similar to the local tetrahedral environments around M1 in ordered $P2_1/n$ or $C2$ structures, suggesting the presence of ordered domains in this otherwise disordered $C2/c$ structure. To aid in the interpretation of these tetrahedral Al environments, density functional theory (DFT) calculations have been performed using two approximations of the CaTs crystal structure: fully ordered tetrahedral chains or fully disordered tetrahedral chains. These calculations suggest that the tetrahedral Al site is a sensitive indicator of order-disorder in CaTs. Tetrahedral Al sites in ordered tetrahedral chains (Si-O-Al-O-Si…) are predicted to have only large C_Q, whereas tetrahedral Al sites in disordered systems (Al-O-Al-O-Al…) are predicted to have only small C_Q. Both environments appear to exist in the synthetic CaTs sample in this study. Cation order-disorder has implications for thermobarometry based on CaTs-containing pyroxenes.

The discovery of the new highly distorted tetrahedral site at ultrahigh magnetic field suggests that highly distorted Al sites in silicate minerals may be NMR-invisible in ^{27}Al 3QMAS NMR spectra acquired at lower fields, and these will have been systematically overlooked. This underscores the necessity to collect ^{27}Al NMR spectra of silicates at the highest available magnetic field strength.

Keywords: CaTs, 3QMAS NMR, density functional theory, Si-Al order-disorder, site distortion, aluminous pyroxene, single chain silicate, Rietveld refinement, VOLCAL